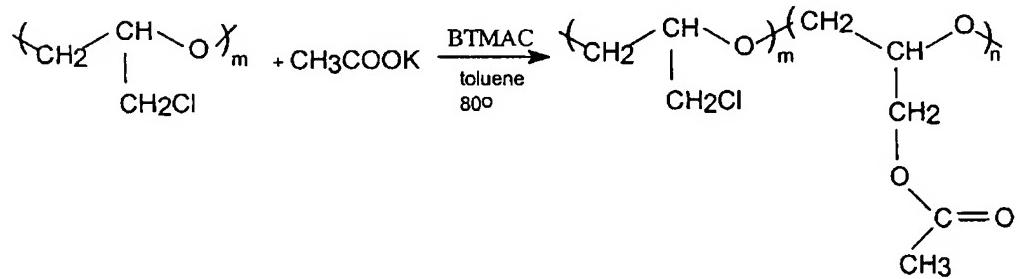


5 **Figure 1.**  $\text{CO}_2$ -philic material design



10

15 **Figure 2.** Modification of poly(epichlorohydrin) with  
acetate groups

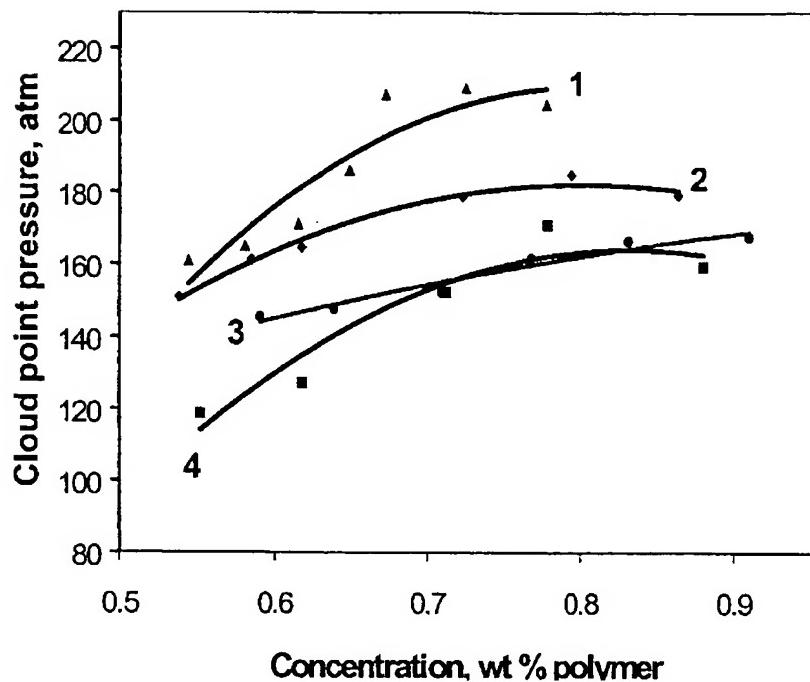


Figure 3. Phase behavior of acetate functionalized epichlorohydrin N = 25 repeat units

- 5 1) 33% acetate  
2) 40 % acetate  
3) PO homopolymer (also 25 repeat units)  
4) 45 % acetate

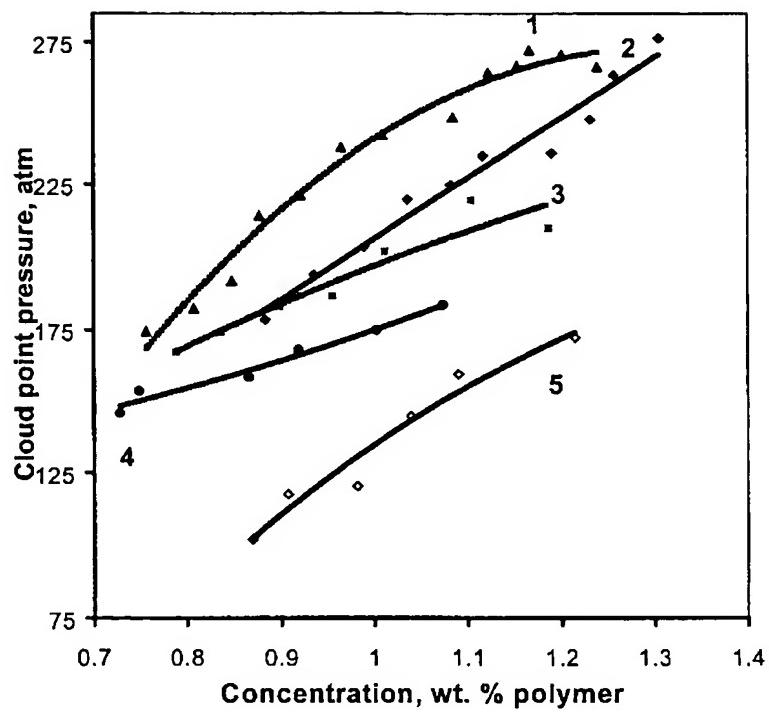


Figure 4. Phase behavior of acetate functionalized poly(epichlorohydrin) N = 7 repeat units

1) Epichlorohydrin homopolymer

5 2) 28 % acetate

3) 100 % acetate

4) 33 % acetate

5) 38 % acetate

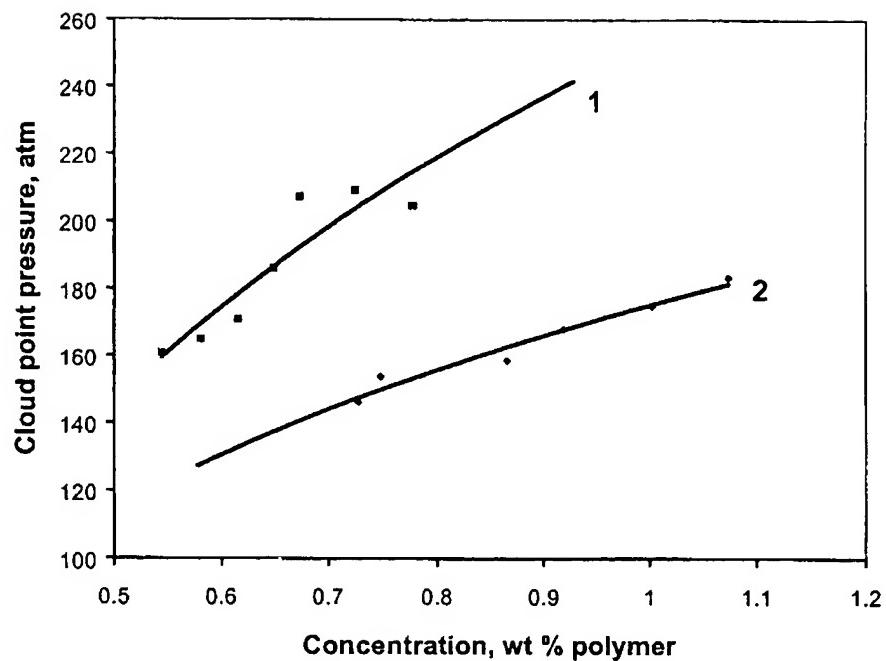
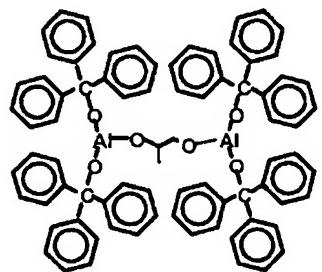
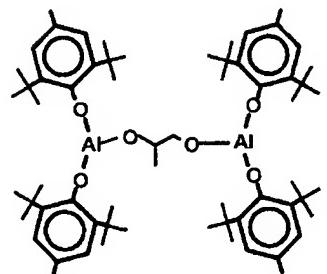
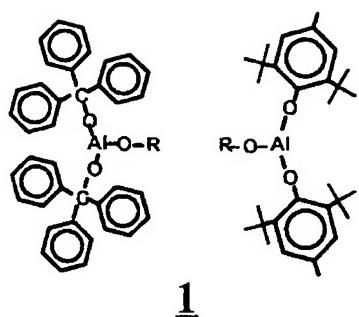


Figure 5. Phase behavior of functionalized poly(epichlorohydrin) with 33 % acetate

1) N = 25 repeat units

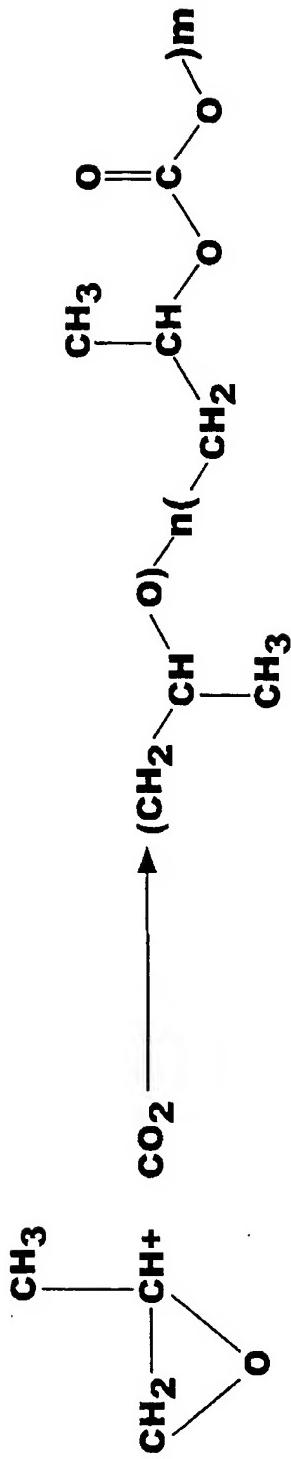
5 2) N = 7 repeat units



2

Figure 6. Sterically hindered aluminum catalysts used in the copolymerization of cyclic ethers and carbon dioxide

## SYNTHESIS OF PO/CO<sub>2</sub>COPOLYMERS



### Conditions

**Catalysts:**  $\begin{matrix} \text{ArO} \\ | \\ \text{Al}-\text{O}-\text{CH}_2\text{CH}-\text{O}-\text{Al}'-\text{OAr} \end{matrix}$  or  $\begin{matrix} \text{Ar}_3\text{C}-\text{O} \\ | \\ \text{O}-\text{Al}-\text{O}-\text{R} \end{matrix}$

[M]=2.5 mol/l  
[Cat]=4.11\*10<sup>-2</sup> mol/l  
24 h at 40-60°C

Figure 7

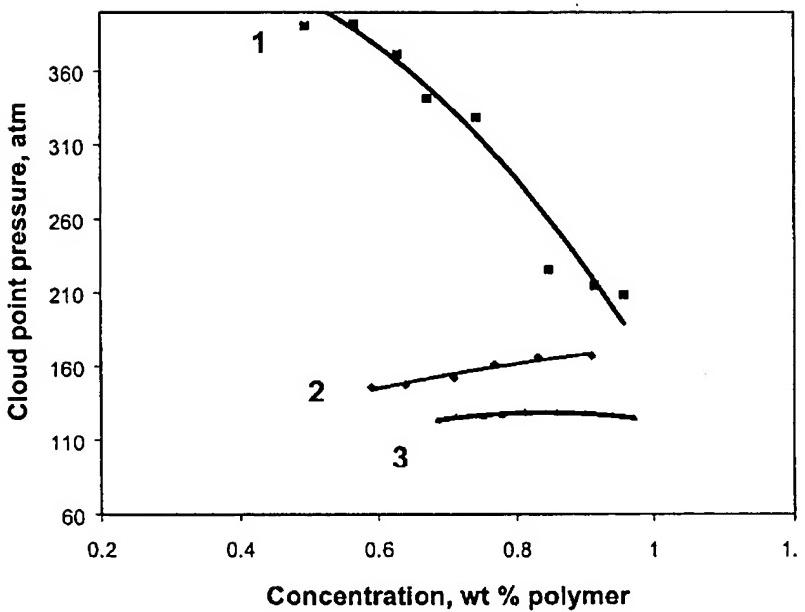


Figure 8. Phase behavior of PO-CO<sub>2</sub> copolymer with N = 25 repeat units

1) PO/CO<sub>2</sub> copolymer 56 % carbonate

5 2) PO homopolymer

3) PO/CO<sub>2</sub> copolymer 40% carbonate

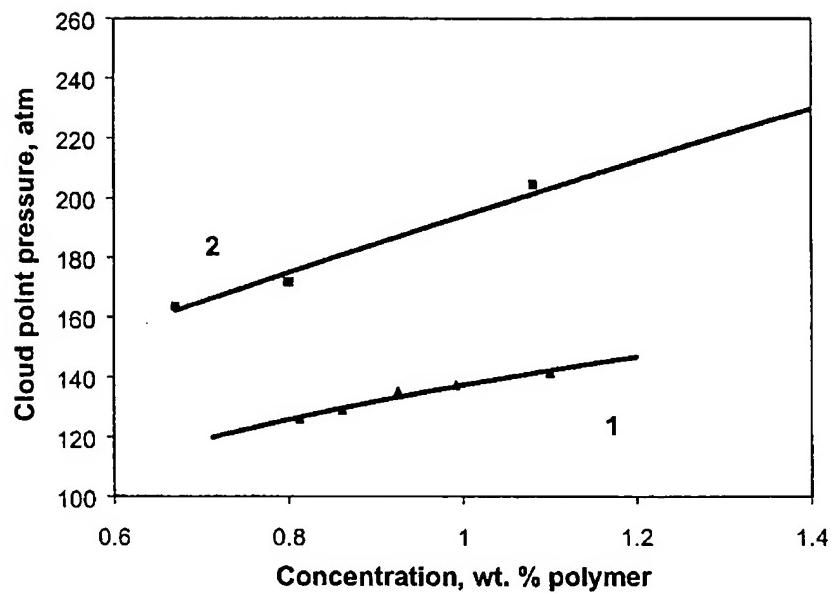


Figure 9. Phase behavior of PO-CO<sub>2</sub> copolymers vs. poly(fluoroether)

1) PO/CO<sub>2</sub> copolymer N = 220 repeat units, 15% carbonate

5 2) Krytox, N = 176 repeat units (reference 24)

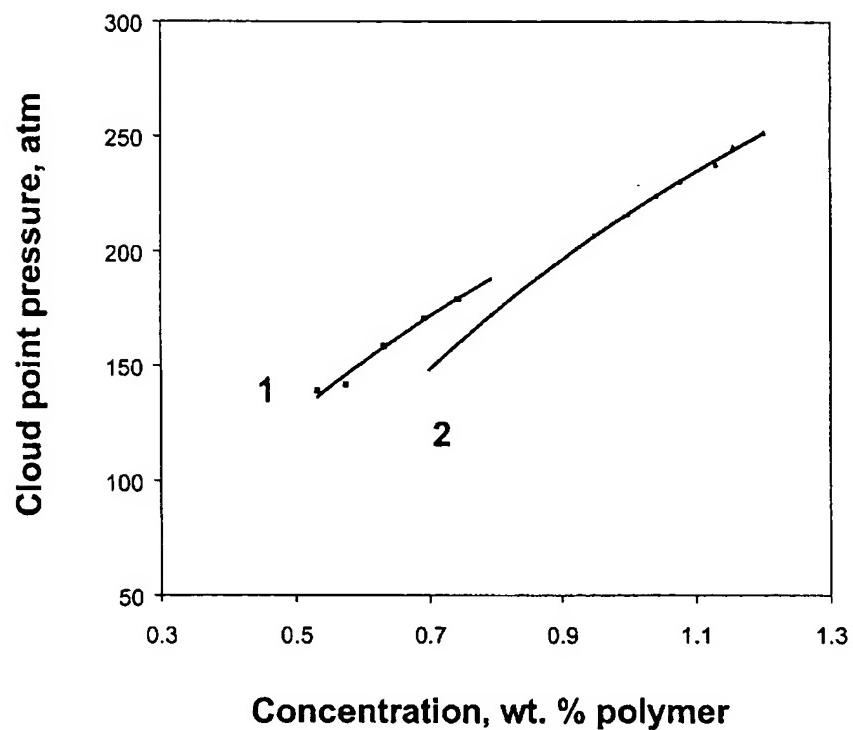


Figure 10. Phase behavior of EO-CO<sub>2</sub> copolymer vs. PEO

1) EO/CO<sub>2</sub> copolymer N = 103; 33.7% carbonate

2) PEO, N = 16

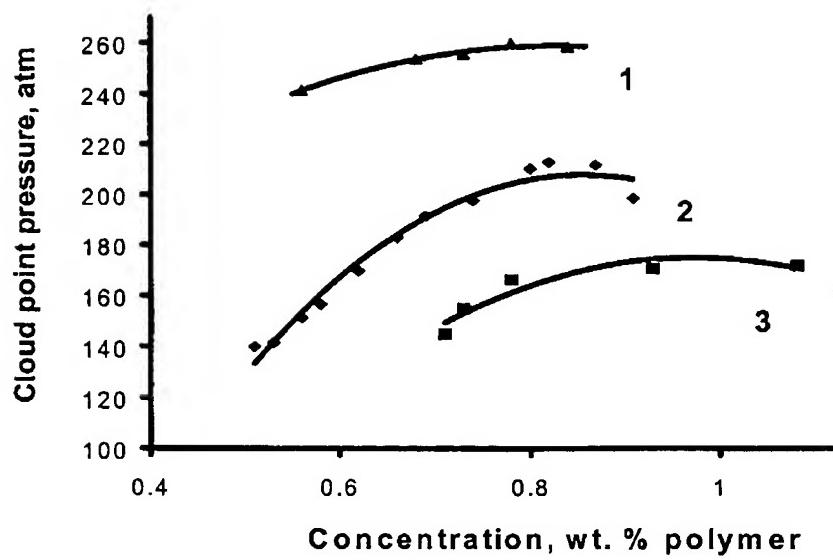


Figure 11. Phase behavior of CHO-CO<sub>2</sub> copolymers with high content of carbonate units

1) 47% carbonate N = 27

5 2) 40% carbonate N = 20

3) 50% carbonate N = 16

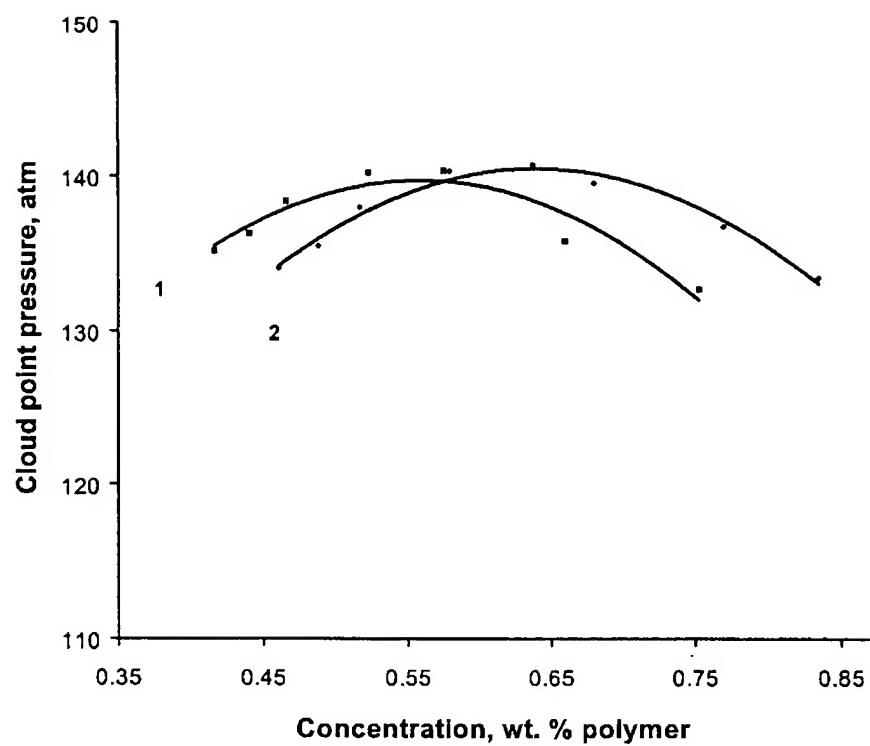


Figure 12. Phase behavior of CHO-CO<sub>2</sub> copolymers with low content of carbonate units

1) 8.8% carbonate N = 124

5 2) 2.3% carbonate N = 88

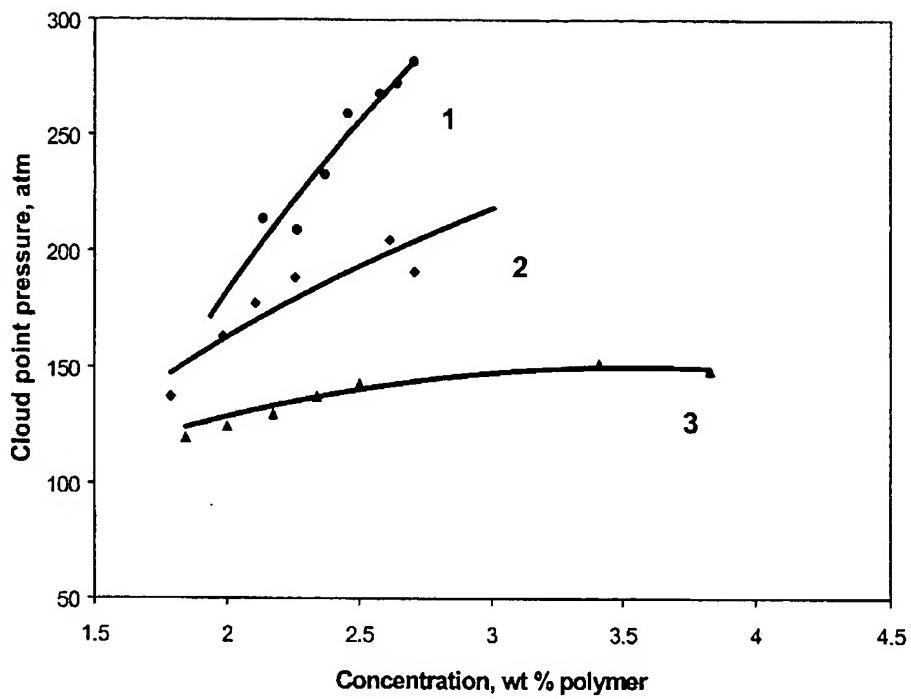


Figure 13. Phase behavior of poly(propylene glycol) diol (1), poly(propylene glycol) monobutyl ether (2) and poly(propylene glycol) acetate (3) with 21 repeat units.

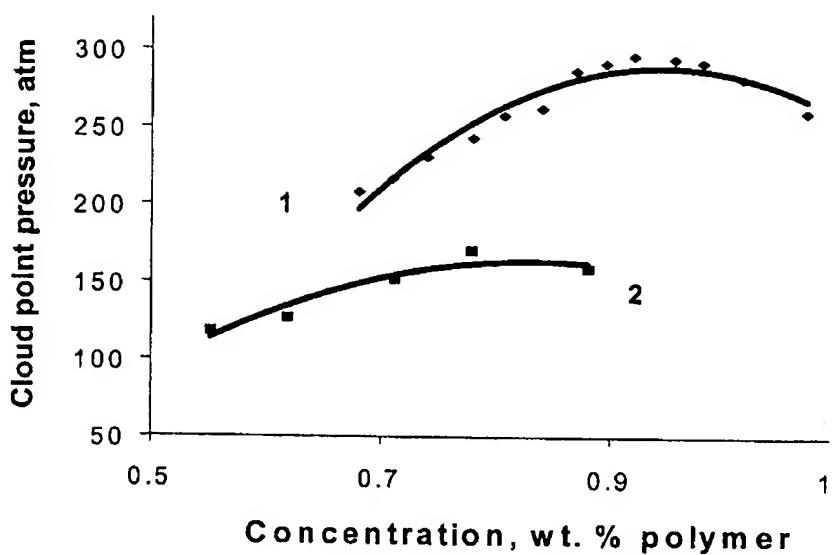


Figure 14. Phase behavior of epichlorohydrin/CO<sub>2</sub> copolymer compared to acetate modified poly(epichlorohydrin)

1) ECH/CO<sub>2</sub> copolymer

5      N = 17

25 % carbonate

2) Modified PECH

N = 25

45 % acetate

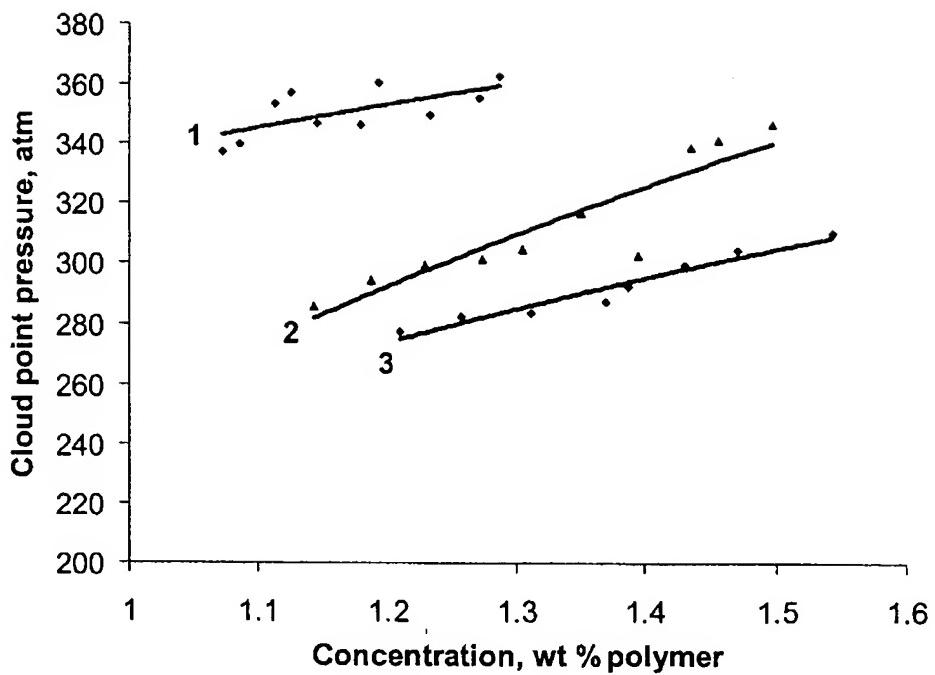


Figure 15. Phase Behavior of Vinyl Acetate and Ethyl Vinyl Ether Homopolymers

- 1) Poly(Vinyl acetate) with 90 SRU
- 2) Poly(Ethyl Vinyl Ether) with 20 SRU
- 3) Poly(Vinyl acetate) with 70 SRU

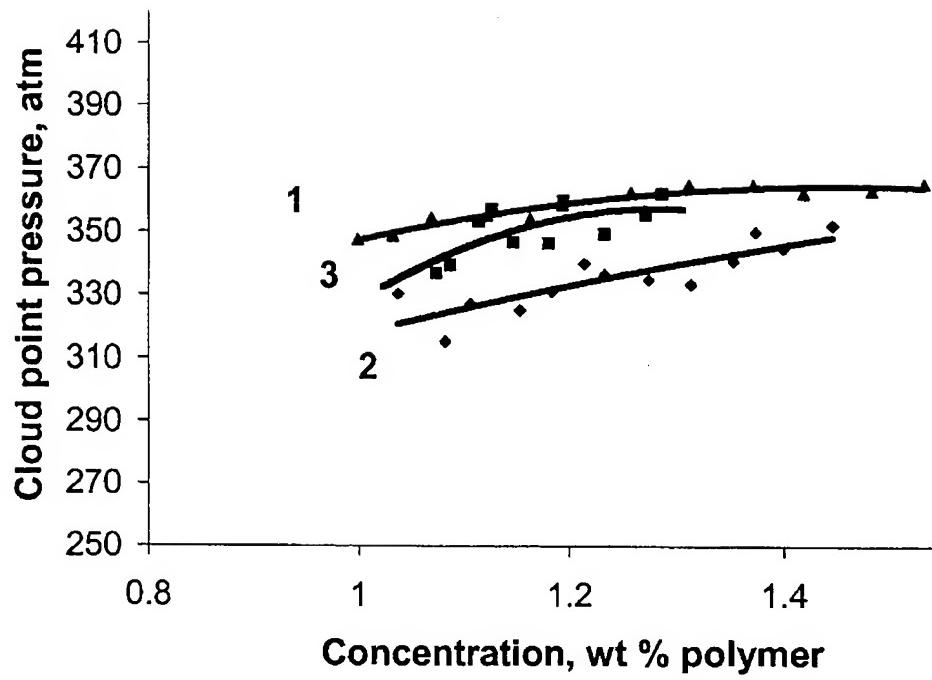
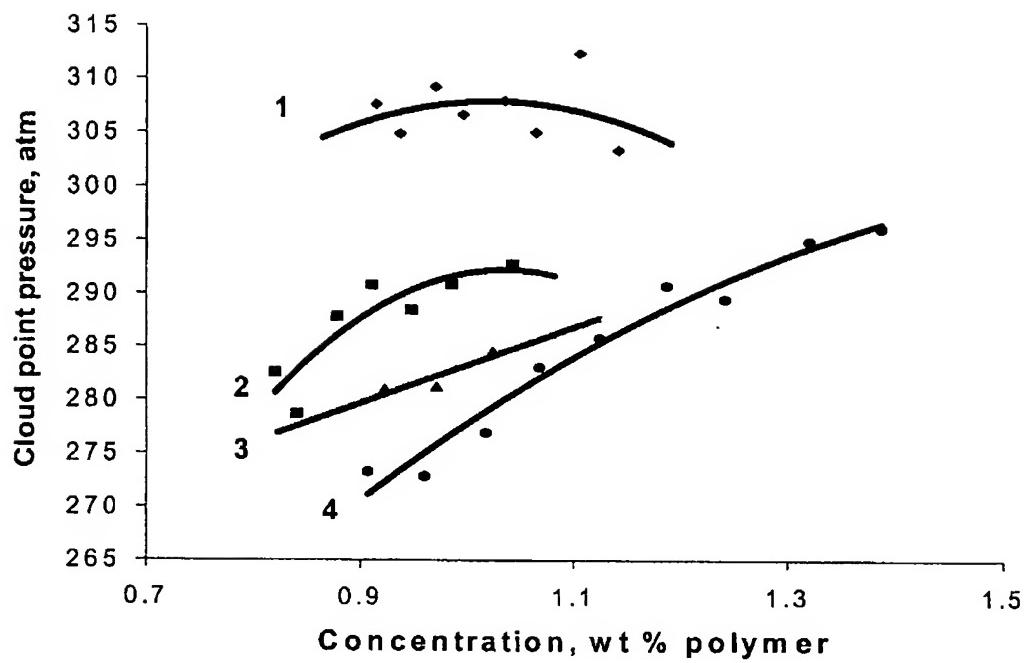


Figure 16. Phase Behavior of Vinyl Acetate/Ethyl Vinyl Ether Copolymers with 90 SRU  
1) 39.8 % VA  
2) 22.4 % VA  
3) VA homopolymer



5      **Figure 17.** Phase Behavior of Vinyl Acetate/Ethyl Vinyl  
Ether Copolymers with 70 SRU

- 1) 67 % VA
- 2) 63 % VA
- 3) VA homopolymer

10     4) 18.47 % VA

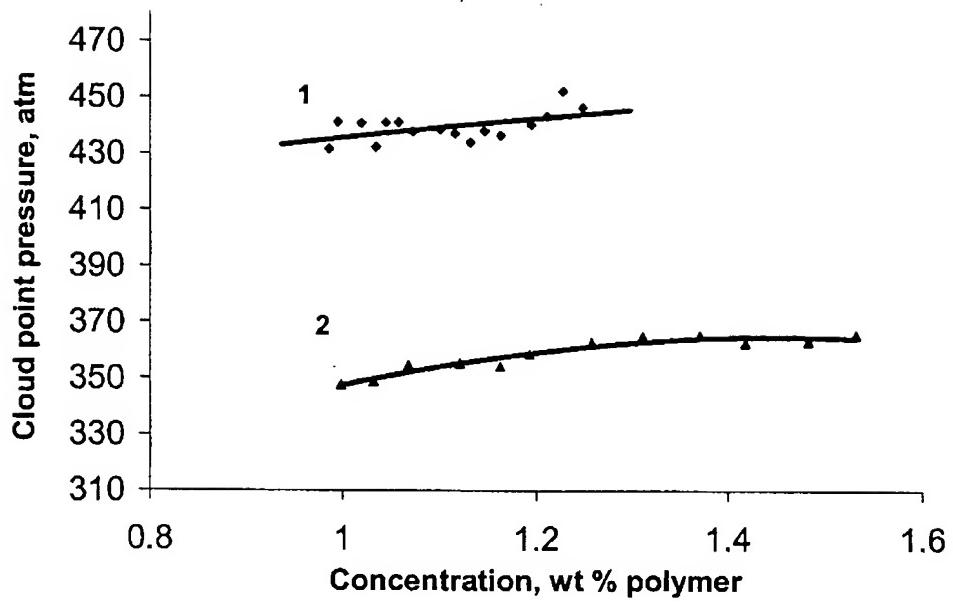
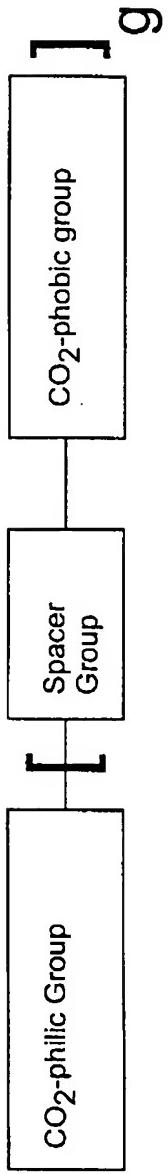


Figure 18. Phase Behavior of Vinyl Acetate/Ethyl Vinyl Ether Copolymers

1) 135 SRU, 46.6 % VA

5 2) 90 SRU, 39.8 % VA



(Reactive Functional Group)[(Monomer 1)<sub>x</sub>(Monomer 2)<sub>y</sub>](End Group)

Figure 19